SPECIFICATION

[Claims]

[Claim 1] A polarizable electrode, comprising a carbon fiber or a carbon powder on a surface of which a concentration of an acidic functional group is 1.0 meq/g or less.

[Claim 2] The polarizable electrode as set forth in Claim 1, wherein said carbon fiber or carbon powder is an activated carbon having a specific surface area of 500 m^2/g or more.

[Claim 3] The polarizable electrode as set forth in Claim 1, wherein said concentration of the acidic functional group is 0.2 meq/g or less.

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[Claim 4] A method of producing a polarizable electrode, characterized in that a concentration of an acidic functional group on a surface of a carbon fiber or a carbon powder is allowed to be 1.0 meq/g or less by reducing said carbon fiber or the carbon powder.

[Detailed Description of the Invention]

Industrial Field of Application

The present invention relates to a carbon fiber or a carbon powder for a polarizable electrode to be used in an electric double layer capacitor, a cell and the like and a method of producing the same.

Prior Art

An energy storage device such as an electric double layer capacitor in which a carbon material, particularly, an activated carbon fiber or an activated carbon powder is used as a polarizable electrode has already been known. In such an energy storage device, a reaction forming electric double layers is primarily performed on a surface of the polarizable electrode comprising the carbon material by absorb-desorbing a positive or negative ion whereupon collection of electric charges in such a portion as described above becomes a reaction at one of the electrodes.

Illustrative examples of constitutions of the energy storage devices of this type which have been developed are shown in FIGS. 4 and 5. Namely, FIG. 4 shows a coil type capacitor comprising polarizable electrodes 10, 11 each comprising an activated carbon fibrous fabric, aluminum current collecting electrodes 12, 13 respectively disposed on these polarizable electrodes, a separator 14, a cover 15, a case 16, and a gasket 17; on this occasion, the polarizable electrodes 10, 11 and the separator 14 are impregnated with an electrolytic solution. FIG. 5 shows a type in which a positive electrode 20 uses a same activated carbon fabric as that shown in FIG. 2 as a polarizable electrode and has an aluminum current collecting layer 21 while a negative electrode uses a lithium-doped Sn-Pb alloy 22 and which comprises a separator 23, a case 24, a cover 25, and a gasket 26. The electrolytic solution which contains a lithium salt as an electrolyte is used.

Not only a type using the activated carbon fiber, but also a type constituted to be of a same coin type as that described above by using activated carbon powders or a mixture of such activated carbon powders and a binder and, further, a winding type are also known. In either type, a specific surface area of a carbon material governs a capacity value.

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Problems that the Invention is to Solve

An electric double storage capacity C to be formed on such a carbon electrode as described above is expressed by the following formula:

$$C = \varepsilon \frac{s}{l}$$

wherein

s represents a specific surface area of a carbon material;

l represents a thickness of an electric double layer; and

ε represents a dielectric constant of an electrolytic solution.

It is appreciated from this formula that an energy storage device having a large capacity can be obtained by using a carbon material having a large specific surface area such as an activated carbon as an electrode. As for a factor to govern characteristics of the energy storage device, there, besides, is a surface chemical structure of the carbon material.

A surface of the activated carbon has a structure, as shown below, that a functional group such as -COOH, -OH, >C=O or the like exists in a polymer of a carbonic 6-member ring.

COOH
OH
O
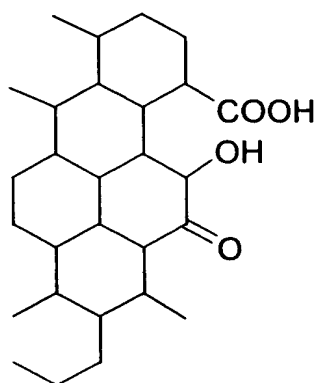
Also, in order to form a genuine electric double layer on the surface of the activated carbon, it is preferable that a number of such polar functional groups is as small as possible whereby a capacity of an electric double layer capacitor in which these polar functional groups are used as a polarizable electrode becomes large. Further, since an acidic functional group such as -COOH, -OH or the like reacts with the electrolytic solution to generate a cation substitution or a decarboxylation, a direct leakage current of the capacitor to be derived from a current generated by such a reaction (hereinafter also referred to as reaction current) as described above becomes large resulting in an increase of a self-discharge.

Means for Solving the Problems

According to the present invention, a polarizable electrode is constituted by a carbon fiber or carbon powder in which a concentration of an acidic functional group such as -COOH, -OH or the like is 1.0 meq/g or less.

Operations

Since the present invention uses a carbon material having a low concentration of an acidic functional group as a polarizable electrode, a direct leakage current of an energy storage device to be obtained is low whereby a self-discharge is also suppressed to be minimal. Further, an extent to which a formation of an electric double layer is hampered is decreased by an existence of a functional group and, on this occasion, when a carbon material having a same specific surface area is used, a capacity to be obtained becomes large.

FIG. 1 shows a relationship between a concentration of an acidic functional group on a surface of an employed activated carbon fiber and a direct leakage current in a capacitor having a structure as shown in FIG. 4. In this case, the direct leakage current is expressed as a value at 2.8 V for 60 minutes; a diameter of the electrode is 5 mm; a phenolic resin type novolak activated carbon fibrous fabric having a measured weight of 100 g/m^2 is used as an activated carbon electrode. Further, measurement of the concentration of the acidic functional group on the surface of the activated carbon is performed by a method as described below. Namely, 500 mg of an activated carbon fibrous fabric is immersed in 30 ml of a 0.2N NaOH aqueous solution and the resultant mixture is subjected to a shaking treatment at a room temperature for a whole day. 10 ml of a supernatant liquid separated from the thus shaken mixture by a centrifuge

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is titrated by a 0.2N HCl aqueous solution to determine an NaOH concentration thereby knowing a gram equivalent number of Na adsorbed by the activated carbon. This gram equivalent number which corresponds to an equivalence of the -COOH group or -OH group on the activated carbon surface is converted to an equivalence of the functional group per 1 g of the activated carbon.

As shown in FIG. 1, the smaller a quantity of the -COOH group or -OH group which the activated carbon has, the lower the direct leakage current of the capacitor. This, as described above, is considered to be derived from the current generated by the reaction between the functional group and the electrolytic solution; on this occasion, the lower the concentration of the functional group, the better. The value thereof is preferably 1.0 meq/g or less, and more preferably 0.2 meq/g or less.

FIG. 2 shows a relationship between a concentration of an acidic functional group and a capacity of a capacitor, and FIG. 3 shows a relationship between a concentration of an acidic functional group and an impedance (value at 1 KHz) of a capacitor; in either case, as the concentration of the functional group becomes lower, the capacitor having better characteristics can be obtained.

As described above, various types of methods of obtaining an activated carbon having a lower concentration of an acidic

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functional group are considered; specific contents thereof will be described in embodiments below.

Examples

Example 1

100 g/m² of a deposition weight of a phenolic resin type activated carbon fibrous fabric (having 2000 m²/g of a specific surface area) was subjected to a heating treatment in a nitrogen stream at a flow rate of 2 l/min and a temperature of 500°C, 800°C or 1000°C for 1 hour. Then, an aluminum layer (300 μm thick) was formed on a side of the thus heat-treated activated carbon fibrous fabric by a plasma spray coating method and then the resultant fabric having an aluminum layer formed thereon was subjected to a punching operation such that it was formed in a circular shape of 5 mm diameter to be used as an electrode. A pair of such circular electrodes and a separator were used to constitute a capacitor as shown in FIG. 4. A solution in which tetraethyl ammonium was dissolved in propylene carbonate was used as an electrolytic solution.

Example 2

100 g/m² of a deposition weight of a phenolic resin type activated carbon fibrous fabric was immersed in a 1N aqueous solution of hydralazine hydrochloride and boiled for 1 hour. The thus treated fabric was rinsed with water and then dried

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and thereafter was used for constructing a capacitor having a same constitution as that of Example 1.

Example 3

100 g/m^2 of a deposition weight of a phenolic resin type activated carbon fibrous fabric was exposed to a hydrogen gas stream at a flow rate of 2 l/min and a room temperature for 10 minutes. The thus obtained activated carbon fabric was used for constructing a capacitor having a same constitution as that of Example 1.

Various characteristics of capacitors obtained in Examples 1, 2 and 3 are shown in Table 1. On this occasion, the capacity shows a value at the time of 1 mA discharge; the leakage current shows a value at 2.8 V for 60 minutes; further, the impedance shows a value at 1 KHz.

Table 1

| | | Capacitor characteristics | | | Concentration of acidic functional group in activated carbon (meq/g) |
		Capacity (F)	Leakage current (μA)	Impedance (Ω)	
Example 1	Treatment at 500°C	0.27	50	40	08
	Treatment at 800°C	0.28	20	35	0.2
	Treatment at 1000°C	0.3	10	30	0.1
Example 2		0.28	15	35	0.2
Example 3		0.28	15	35	0.2
Conventional Example		0.25	100	50	1.2

Example 4

A carbon fiber having a specific surface area of 500 m^2/g was treated at a temperature of 500°C, 800°C or 1000°C in a same manner as in Example 1. Then, an aluminum layer (300 μm thick) was formed on a side of the thus treated carbon fiber by a plasma spray coating method and then the resultant fiber having an aluminum layer formed thereon was subjected to a punching operation such that it was formed in a circular shape of 5 mm diameter. The thus formed fiber was used as a positive electrode whereas a lithium-doped Sn-Pb alloy was used as a negative electrode whereby an energy storage device having a constitution as shown in FIG. 5 was constructed. Characteristics of the energy storage device thus obtained in Example 4 are shown in Table 2.

Table 2

	Characteristics			Concentration of acidic functional group in activated carbon (meq/g)
	Capacity (F)	Leakage current (μA)	Impedance (Ω)	
Treatment at 500°C	1	30	70	0.8
Treatment at 800°C	1.3	20	60	0.2
Treatment at 1000°C	1.5	10	50	0.1
Conventional Example	1	50	100	1.2

Since an electric double layer formation on the carbon surface of any one of the above-described 2 types of each of the carbon fiber and carbon powder for use in the present invention is a rate-determining factor of an electrode reaction, the larger the specific surface area thereof, the more desirable; on this occasion, it is practically preferable that the specific surface area is 500 m^2/g or more. From this standpoint, as for materials having a high specific surface area and strength, a phenolic type novolak resin, PAN, cellulose and pitch are appropriate.

Further, as for reduction methods of the activated carbon, methods using a hydrazine hydrochloride solution and a hydrogen gas were respectively described above. There, besides, are a method of using a chemical reducing agent such as $NaBH_4$ hydrochloride, $LiAlH_4$ or the like and a method of contacting it with a reducing gas such as OC, a hydrocarbon or the like. Furthermore, in regard to the carbon powder, a similar action effect to that described above was obtained.

Advantage of the Invention

As described above, according to the present invention, a polarizable electrode which is capable of providing an energy storage device such as an electric double layer capacitor having a low direct leakage current and impedance and a large capacity can be obtained.

[Brief Description of Drawings]

FIG. 1 is a graph showing a relationship between a concentration of an acidic function and a leakage current of a capacitor; FIG. 2 is a graph showing a relationship between a concentration of an acidic functional group in an activated carbon fiber and a capacity of a capacitor; FIG. 3 is a graph showing a relationship between a concentration of an acidic functional group in an activated carbon fiber and an impedance of a capacitor; FIG. 4 is a longitudinal sectional view showing
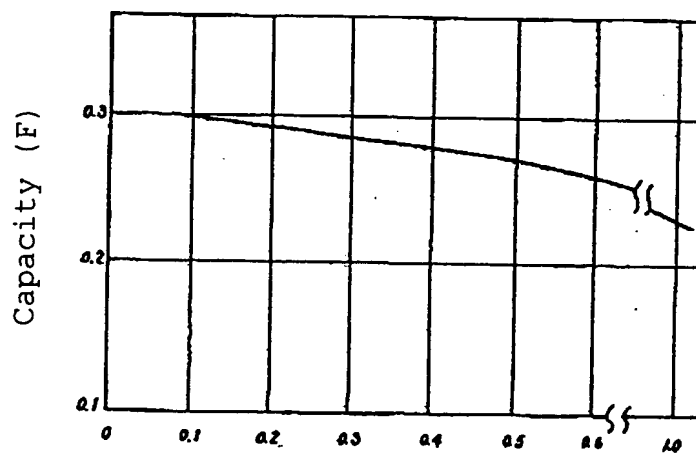
an example of a constitution of a capacitor; and FIG. 5 is a
longitudinal sectional view showing an example of a constitution
of an energy storage device comprising an activated carbon fiber
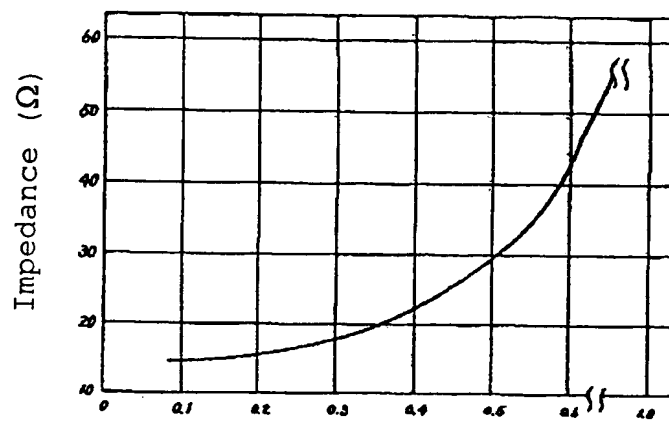and a non-polarizable electrode.

[Figure 1]
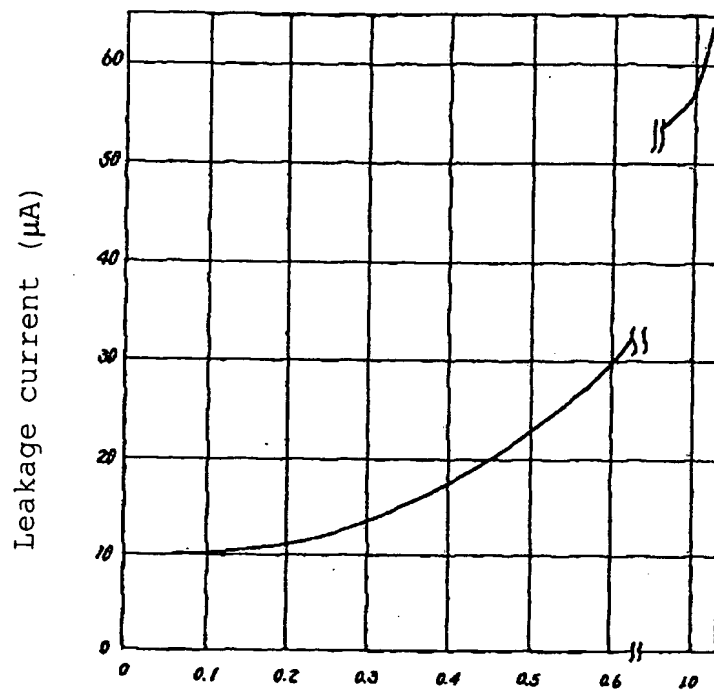
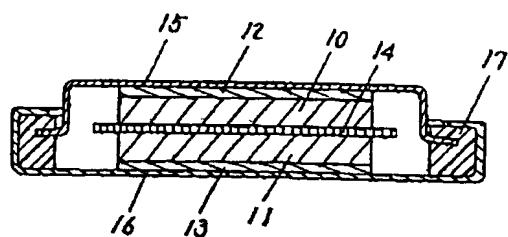Concentration of acidic functional group (meq/g)

[Figure 2]

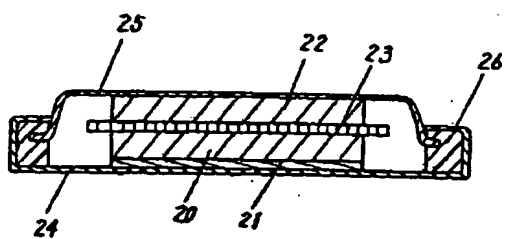Concentration of acidic functional group (meq/g)

[Figure 3]

Concentration of acidic functional group (meq/g)

[Figure 4]

[Figure 5]

(54)【発明の名称】　分極性電極およびその製造方法

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【特許請求の範囲】

【請求項1】表面の酸性官能基の濃度が1．0ミリ当量／g以下の炭素繊維または炭素粉末より成る分極性電極。

【請求項2】前記炭素繊維、炭素粉末が比表面積500m²／g以上の活性炭素である特許請求の範囲第1項記載の分極性電極。

【請求項3】前記表面酸性官能基の濃度が0．2ミリ当量／g以下である特許請求の範囲第1項記載の分極性電極。

【請求項4】炭素繊維または炭素粉末を還元することにより、その表面酸性官能基の濃度を1．0ミリ当量／g以下にすることを特徴とする分極性電極の製造方法。

【発明の詳細な説明】

産業上の利用分野

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本発明は、電気二重層キャパシタ、電池などに用いる分極性電極のための炭素繊維、炭素粉末およびその製造法に関するものである。

従来の技術

炭素材料、特に活性炭繊維、活性炭粉末を分極性電極として用いる電気二重層キャパシタなどのエネルギ貯蔵装置は既に知られている。このようなエネルギ貯蔵装置においては、炭素材料から成る分極性電極の表面で、正または負イオンの吸脱着による電気二重層の形成反応が主に起きており、この部分での荷電の蓄積が一方の電極反応となる。

現在までに開発されているこの種のエネルギ貯蔵装置の代表的な構成例を第4図，第5図に示す。すなわち、第4図に示すものは、活性炭繊維布より成る分極性電極10，11と、この上のアルミニウム集電極12，13、

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セパレータ１４、蓋１５、ケース１６、ガスケット１７
から成るコイル型のキャパシタであり、分極性電極１
０，１１、セパレータ１４には電解液が含浸されてい
る。また第５図に示すものは、正極２０が、第２図と同
じ活性炭布を分極性電極とし、アルミニウム集電層21を
有し、負極は、リチウムをドーピングシタSn−Ｐｂ合金
２２を用いたもので、セパレータ２３、ケース２４、蓋
２５、ガスケット２６により構成される。電解液にはリ
チウム塩を電解質としたものを用いている。
活性炭繊維を用いるものの他に、活性炭粉末もしくは、
これとバインダとの混合物を用いて上記と同じコイン型
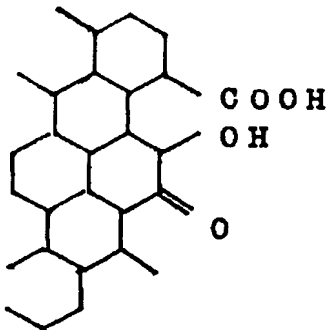に構成したものや、捲回型のものも知られており、いず
れの場合も炭素材料の比表面積が容量値を支配する。
発明が解決しようとする問題点
上記のような炭素電極上に形成される電気二重蓄積容量
Ｃは次式で表わされる。

$$C = \varepsilon \frac{s}{\ell}$$

ここでｓは炭素材料の比表面積、１は電気二重層の厚
さ、εは電解液の誘電率である。この式から比表面積が
大きな炭素材料、すなわち活性炭のような材料を電極に
用いることにより大容量のエネルギ貯蔵装置が得られる
ことがわかる。エネルギ貯蔵装置の特性を支配する因子
として、この他に炭素材料の表面化学構造がある。
活性炭の表面は以下に示すように炭素６員環の重合体に
−ＣＯＯＨ，−ＯＨ，＞Ｃ＝Ｏなどの官能基が存在す
る。

そして活性炭表面に純粋な電気二重層を形成するために
は、これらの極性官能基ができるだけ少ない方が好まし
く、これらを分極性電極として用いた電気二重層キャパ
シタの容量が大きくなる。さらに−ＣＯＯＨ，−ＯＨな
どの酸性官能基と電解液とが反応して陽イオン置換や、
脱炭酸反応が起きるため、その反応電流に起因してキャ
パシタの直流漏れ電流も大きくなり、自己放電の増大に
つながる。
問題点を解決するための手段
本発明は、表面の−ＣＯＯＨや−ＯＨのような酸性官能
基の濃度が１．０ミリ当量／ｇ以下の炭素繊維、または
炭素粉末により分極性電極を構成するものである。

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作用
本発明では、酸性官能基濃度が低い炭素材料を分極性電
極として用いるため、得られるエネルギ貯蔵装置の直流
漏れ電流が低く、自己放電も最少におさえられる。ま
た、電気二重層形成が官能基の存在により妨げられるこ
とも少なくなり、同一の比表面積の炭素材料を用いた
時、得られる容量は大きくなる。
第１図は、第４図の構成のキャパシタにおいて、用いる
活性炭繊維の表面酸性官能基濃度と直流漏れ電流との関
係を示すものである。ここで直流漏れ電流は２．８Ｖ６
０分値であり、電極の直径は５㎜、活性炭電極は坪量１
００ｇ／㎡のフェノール樹脂系ノボラック活性炭繊維布
を用いた。また活性炭の表面酸性基濃度の測定は、次の
方法によった。すなわち、５００㎎の活性炭繊維布を
０．２Ｎ NaOH水溶液３０ｍｌの中に浸漬し、一昼夜室温
で振とうする。遠心分離により分離した上澄液１０ｍｌを
０．２NHCｌで滴定し、NaOHの濃度を測定することに
より活性炭に吸着されたＮａのグラム当量数を知る。こ
のグラム当量数が活性炭表面の−ＣＯＯＨ，−ＯＨ基の
当量に相当し、これを１ｇ活性炭当たりの官能基当量に
換算する。
第１図のように、−ＣＯＯＨ，−ＯＨ基の量の少ない活
性炭ほどキャパシタの直流漏れ電流が低くなる。これは
既述のように、これらの官能基と電解液との反応電流に
起因するものと考えられ、官能基濃度が低いほど好まし
い。その値は１．０ミリ当量／ｇ以下、さらに好ましく
は０．２ミリ当量／ｇ以下である。
第２図は酸性官能基濃度とキャパシタの容量、第３図は
官能基濃度とキャパシタのインピーダンス（１ＫＨｚでの
値）との関係を示すが、いずれも官能基濃度が低い方が
優れた特性のキャパシタが得られる。
このように酸性官能基濃度の低い活性炭を得る方法は種
々考えられ、その具体的内容については以下の実施例で
述べる。
実施例
実施例１
目付１００ｇ／㎡のフェノール樹脂系活性炭繊維布（比
表面積２０００㎡／ｇ）を、窒素気流２■／分中５００
℃，８００℃または１０００℃で１時間熱処理する。得
られた熱処理活性炭繊維布の片面にプラズマ容射法によ
りアルミニウム層（厚さ３００μｍ）を形成し、これを
直径５㎜の円形に打抜き電極とする。一対の円形電極と
セパレータを用いて第４図のようなキャパシタを構成す
る。電解液はプロピレンカーボネートにテトラエチルア
ンモニウムパークロレートを溶解したものを用いた。
実施例２
目付１００ｇ／㎡のフェノール樹脂系活性炭繊維布を、
１Ｎ塩酸ヒドラジン水溶液中に浸漬し、１時間煮沸す
る。水洗乾燥後、実施例１と同じ構成のキャパシタを組
立てる。

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実施例3

目付100g／㎡のフェノール樹脂系活性炭繊維布を、室温下2■／分の水素ガス気流中に10分間さらす。得られた活性炭布を実施例1と同じ構成のキャパシタに組立てる。

第1表に実施例1，2，3で得られたキャパシタの諸特性を示す。なお容量は1mA放電時の値、漏れ電流は2.8V60分値、インピーダンスは1KHzでの値である。

第　　　1　　　表

| | | キャパシタ特性 | | | 活性炭中の酸性官能基濃度 |
		容量(F)	漏れ電流(μA)	インピーダンス(Ω)	(ミリ当量/g)
実施例1	500℃処理	0.27	50	40	0.8
	800℃処理	0.28	20	35	0.2
	1000℃処理	0.3	10	30	0.1
実施例2		0.28	15	35	0.2
実施例3		0.28	15	35	0.2
従来例		0.25	100	50	1.2

実施例4

比表面積500㎡／gの炭素繊維を実施例1と同じく500℃，800℃または1000℃で処理し、片面にプラズマ溶射によりアルミニウム層（厚さ300μm）を形成し、これを直径の5mmの円形に打抜く。これの正極に用い、負極にリチウムをドーピングしたSn−Pb合金を用いて第5図に示す構成のエネルギ貯蔵装置を組立てる。

第2表に実施例4で得られたエネルギ貯蔵装置の特性を示す。

第　　　2　　　表

| | 特性 | | | 活性炭中の酸性官能基濃度 |
	容量(F)	漏れ電流(μA)	インピーダンス(Ω)	(ミリ当量/g)
500℃処理	1	30	70	0.8
800℃処理	1.3	20	60	0.2
1000℃処理	1.5	10	50	0.1
従来例	1	50	100	1.2

本発明で用いる炭素繊維，炭素粉末は、既述の2つの型

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のいずれにおいても炭素の表面の電気二重層形成が電極反応の律速になっているため、その比表面積が大きいことが望ましく、実用的に500㎡／g以上であることが好ましい。この点から、高比表面積でなおかつ強度を有する材料としては、フェノール系ノボラック樹脂、PAN、セルロース，ピッチが適当である。

また活性炭の還元方法として実施例では塩酸ヒドラジン溶液，水素ガスを用いる方法を示したが、この他にも塩酸NaBH4，LiAlH4などの化学還元剤を用いる方法、OCや炭化水素などの還元性ガスと接触させる方法がある。

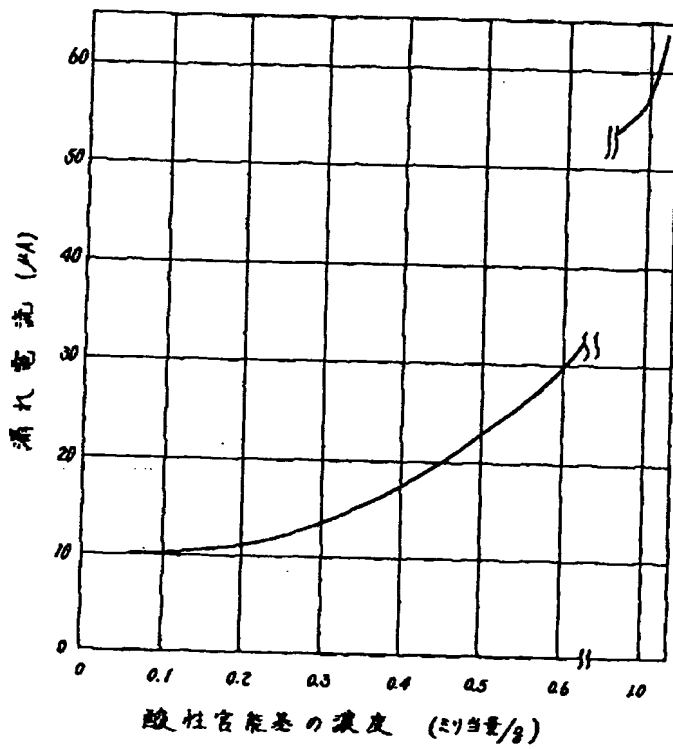また、炭素粉末についても炭素繊維と同様な作用効果が得られた。

発明の効果

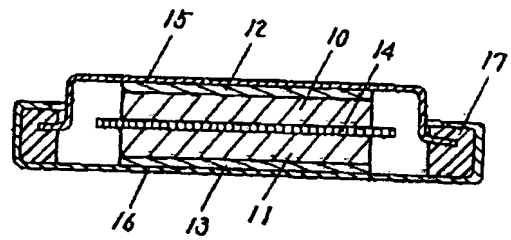以上のように、本発明によれば、直流漏れ電流、インピーダンスが低く、大容量の電気二重層キャパシタなどのエネルギ貯蔵装置を与える分極性電極を得ることができる。

【図面の簡単な説明】

第1図は活性炭繊維中の酸性官能濃度とキャパシタの漏れ電流との関係を示す図、第2図は活性炭繊維中の酸性官能基濃度とキャパシタの容量との関係を示す図、第3図は活性炭繊維中の酸性官能基濃度とキャパシタのインピーダンスとの関係を示す図、第4図はキャパシタの構成例を示す縦断面図、第5図は活性炭繊維と非分極性電極とから構成されるエネルギ貯蔵装置の構成例を示す縦断面図である。
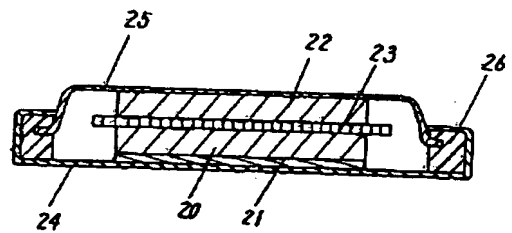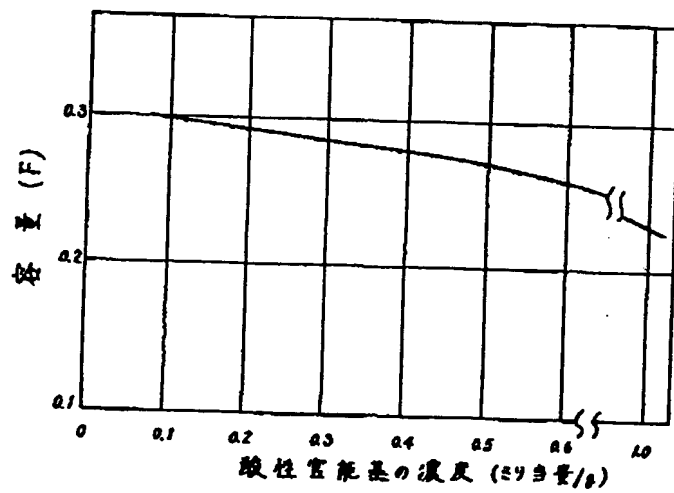
【第1図】

縦軸: 漏れ電流 (μA)　60, 50, 40, 30, 20, 10, 0
横軸: 酸性官能基の濃度 (ミリ当量/g)　0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 1.0

【第4図】

15　12　10　14　17
16　13　11

【第5図】

25　22　23　26
24　20　21

【第2図】

縦軸: 容量 (F)　0.3, 0.2, 0.1
横軸: 酸性官能基の濃度 (ミリ当量/g)　0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 1.0

【第3図】